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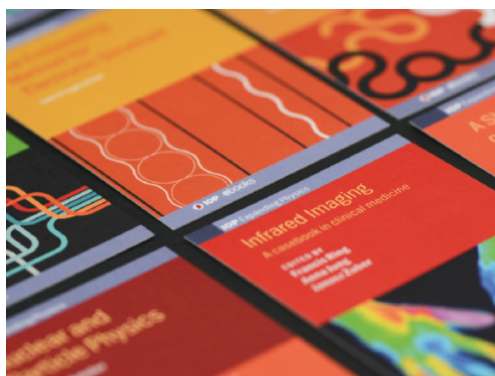
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Scaling out the density dependence of the α relaxation in glass-forming polymers

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Abstract. – We show that the density and temperature dependences of the α -relaxation time of several glass-forming polymers can be described through a single scaling variable $X = e(\rho)/T$, where $e(\rho)$ is well fitted by a power law ρ^x , x being a species-specific parameter. This implies that “fragility” is an intrinsic, density-independent property of a glass-former characterizing its super-Arrhenius slowing-down of relaxations, and it leads us to propose a modification of the celebrated Angell plot.

The glass transition of liquids and polymers is conventionally studied at constant, usually atmospheric, pressure (P) by cooling the system. However, in an effort to disentangle the effects of density (ρ) and temperature (T) that both influence the viscous slowing-down under isobaric conditions and to provide a more stringent test of existing models and theories, there has recently been an increasing number of systematic studies of glass formation using both T and P as experimentally controlled variables. Glass-forming polymers are interesting in this respect: first, because of their rather high compressibility allowing to cover a significant range of densities and second, because of the important role played in polymer science by the free-volume theory that puts the emphasis on congestion effects due to the increase of density as one approaches the glass transition [1].

In this letter we analyze new dielectric relaxation data obtained on several glass-forming polymers up to 3 kbars poly(epichlorhydrine) (PECH), poly(vinylmethylether) (PVME), poly(vinylacetate) (PVAc), poly(methylmethacrylate) (PMMA), and a combination of new dielectric, neutron scattering and calorimetric data on 1,4-poly(butadiene) (1,4-PB). We show

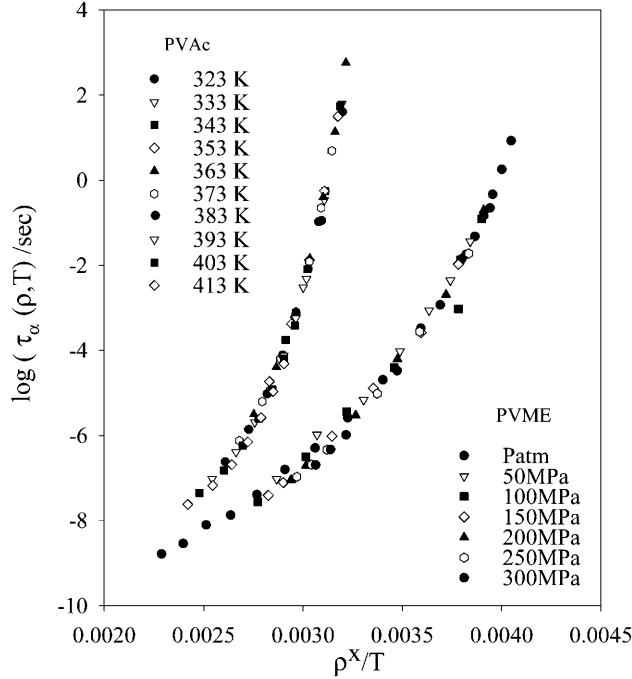


Fig. 1 – Scaled plot of $\log(\tau_\alpha(\rho, T))$ vs. $X = \rho^x/T$ for PVME ($x = 2.7$) and PVAc ($x = 1.4$). Data were obtained at atmospheric pressure and along different isotherms and isobars up to 300 MPa.

that the ρ - and T -dependences of the α -relaxation time (τ_α expressed, say, in seconds) can be described by a single scaling variable $X = e(\rho)/T$,

$$\log(\tau_\alpha(\rho, T)) = F\left(\frac{e(\rho)}{T}\right), \quad (1)$$

where, over the range of densities experimentally accessible, $e(\rho)$ can be fitted by a power law, ρ^x ; the parameter x and the function $F(X)$ are species-specific. This scaling generalizes to polymers work recently done on several molecular liquids. As a spin-off, we show that “fragility”, a concept introduced by Angell [2] to characterize the degree of deviation from Arrhenius behavior in the T -dependence of $\log(\tau_\alpha)$ as one approaches the glass transition, is independent of density and is thus an inherent property of each glass-former. This leads us to suggest a modification of the widely used Angell plot.

As a more extensive data base on the P - and T -dependences of the α -relaxation time (and of the viscosity) of glass-forming polymers and liquids now becomes available [3], and reasonably accurate equations of state exist to convert P, T results to ρ, T results, the question arises of how to best organize the data, in a model-free and physically meaningful manner. In the case of molecular liquids, it has recently been suggested that the ρ -dependence could be described through a single parameter, an effective activation energy $E_\infty(\rho)$ characteristic of the high- T Arrhenius regime, *i.e.*, $\log(\tau_\alpha(\rho, T)) = F(E_\infty(\rho)/T)$. The same procedure, however, is not applicable to glass-forming polymers because most of them cannot be studied at T high enough for reaching an Arrhenius regime, so that $E_\infty(\rho)$ cannot be directly determined. In the cases studied in ref. [4], $E_\infty(\rho)$ was a quite featureless, increasing function of ρ (in the accessible range); rather than using an (uncontrolled) extrapolation of the data at high T ,

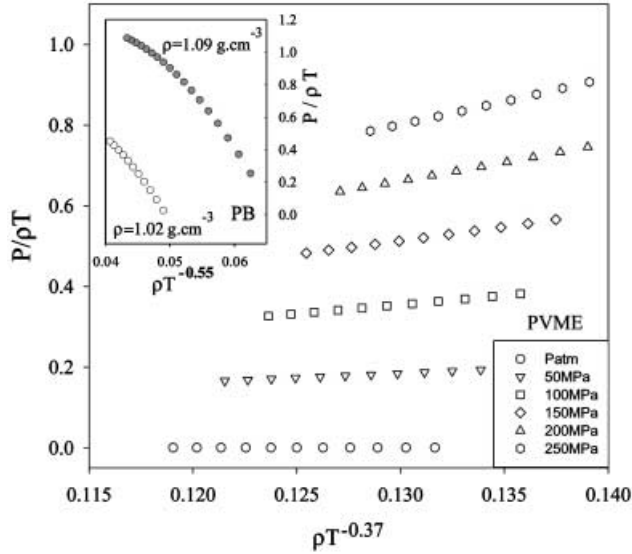


Fig. 2 – Equation of state $P/\rho T$ vs. $X = \rho^x/T$ for PVME calculated from [10] along isobars; inset: 1,4-PB along two isochores. Note the absence of scaling.

it then seems more sensible to choose a simple predefined function of ρ , $e(\rho)$, with as few adjustable parameters as possible, to build a scaling variable $X = e(\rho)/T$. An appealing choice is a one-parameter power law, ρ^x , x being material-specific. Such a choice has been used to represent α -relaxation time data for the fragile glass-forming liquid ortho-terphenyl (o-TP), with $x = 4$ [5]; it is also consistent with a recent study of the density dependence of the glass transition line $T_g(\rho)$ of several polymers (up to few kbars), where it was found that $T_g(\rho)\alpha\rho^x$, with $x \approx 2.0$ for atactic poly(propylene), $x \approx 2.7$ for poly(styrene), and $x \approx 3.4$ for poly(carbonate) [6]. We have thus analyzed the α -relaxation time $\tau_\alpha(\rho, T)$, obtained from dielectric relaxation measurements made on PECH, PVME, PVAc, and PMMA over a wide range of T and P (all experimental details are given in [7–9]) and converted to (ρ, T) via the equation of state proposed by Sanchez and Cho [10], as a function of ρ^x/T , x being an adjustable parameter. As illustrated in fig. 1, a very good scaling of the data is indeed reached. We find $x \approx 2.7$ for PECH and PVME, $x \approx 1.4$ for PVAc, and $x \approx 1.25$ for PMMA. We have applied the same analysis to the α -relaxation time data obtained on 1,4-PB [11] with $x \approx 1.8$. In all cases a good data collapse is found with eq. (1) and $e(\rho) = \rho^x/T$ (see inset of fig. 4 below).

Before discussing some of the consequences of the scaling, it is worth stressing that, despite its appealing form, the power law behavior of $e(\rho)$ may not convey much physical content. For o-TP it was suggested that the ρ^4/T scaling was reminiscent of the well-known scaling property of simple liquids interacting via a soft repulsive pair potential, $v(r) = \epsilon(\frac{\sigma}{r})^n$, with $n = 12$ as in the Lennard-Jones model [12]: indeed, for such systems the long-time properties (α -relaxation time, diffusion coefficient, etc.) depend on ρ and T only through a single combination $\rho T^{-3/n}$, hence for $n = 12$, $\rho T^{-1/4}$, or, equivalently, ρ^4/T . However, such an interpretation implies a strong corollary, that the excess thermodynamic properties of the system (measured with respect to the ideal-gas contribution) should also depend on the scaling variable, $\rho T^{-3/n}$ or $\rho^{n/3}/T$, only. We have checked that this is not the case for any of the polymers considered here (nor for o-TP): as illustrated in fig. 2 for PVME and PB, the quantity $(\frac{P}{\rho T})$ obtained from the

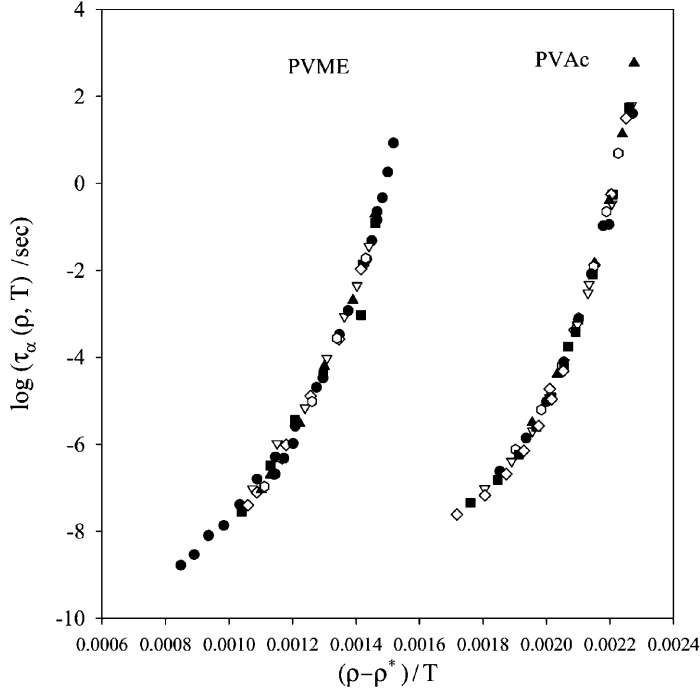


Fig. 3 – Scaled plot $\log(\tau_\alpha(\rho, T))$ vs. $X = e(\rho)/T$ with $e(\rho) = \rho - \rho^*$ for PVME ($\rho^* = 0.62$) and PVAc ($\rho^* = 0.29$); same symbols as in fig. 1.

existing equations of state is not a unique function of ρ^x/T with x determined from the scaling plot of the α -relaxation time. Not unexpectedly, in the available range of ρ , polymers do not behave as soft repulsive spheres. The power law ρ^x should thus be considered as a convenient, one-parameter way of representing the ρ -dependence of the activation energy scale $\propto e(\rho)$, a scale that, when data are available at high enough T , can be identified with the empirical Arrhenius activation energy $E_\infty(\rho)$ [4]. Actually, a good agreement to the α -relaxation time data can also be obtained by choosing a one-parameter linear description, $e(\rho) = \rho - \rho^*$; see fig. 3. Again, no special emphasis should be put on the fact that $e(\rho)$ is a linear function of ρ ; this merely reflects the fact that over the limited range of density that is accessible experimentally, $e(\rho)$ increases monotonically with ρ in a featureless fashion.

Besides the fact that it helps organizing all experimental data obtained by changing P and/or T in a simple and rational way, the main consequence of the scaling expressed by eq. (1) is that “fragility”, which characterizes the super-Arrhenius T -dependence of the τ_α and the viscosity, is an intrinsic property of a glass-former, in that it does not vary with density. The concept of fragility has proved to be most useful in the study of glass-forming liquids and polymers and is now part of the very lexicon of such studies. Quantifying the degree of fragility of a system can be conveniently done without having recourse to fitting formulae by considering the steepness index at constant density, $m_{\rho,\tau}$, defined as

$$m_{\rho,\tau} = \left. \frac{\partial \log(\tau_\alpha)}{\partial \left(\frac{T_\tau}{T}\right)} \right|_\rho (T = T_\tau), \quad (2)$$

where T_τ is the temperature at which $\tau_\alpha = \tau$ (expressed, say, in s) at the given ρ . By using

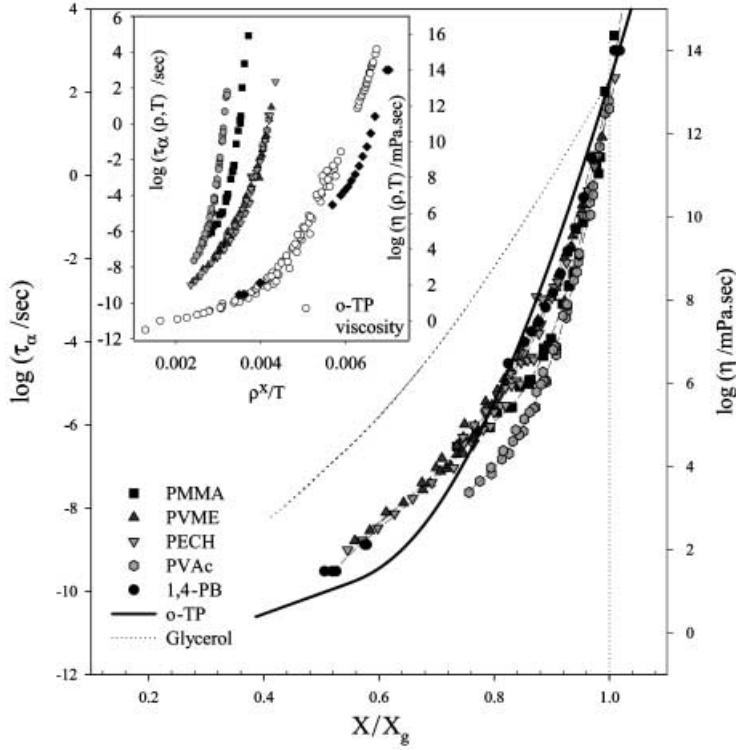


Fig. 4 – Modified Angell plot: $\log(\tau_\alpha)$ vs. X/X_g , where X_g is the glass transition value ($\tau_\alpha = 100$ s) for all polymers shown in inset. For comparison we also show as full and dotted lines the scaled curves for o-terphenyl and glycerol, respectively [4]. The dashed lines are guides for the eye. Inset: scaled plot $\log(\tau_\alpha(\rho, T))$ vs. $X = \rho^x/T$ for several polymers, PVME, PECH ($x = 2.7$), PMMA ($x = 1.25$), PVAc ($x = 1.4$), 1,4-PB ($x = 1.8$) and $\log(\eta(\rho, T))$ for o-terphenyl ($x = 4$).

eq. (1) and defining X_τ as the value of the scaling variable such that $F(X_\tau) = \log(\tau)$, it is easy to show that $m_{\rho,\tau} = X_\tau F'(X_\tau)$, where $F'(X_\tau) = \frac{dF(X)}{dX}$ is *independent of density*. Thus, fragility, when properly defined, is an intrinsic property of the glass-former. Breakdown of this feature may occur when major structural changes take place in the system under compression, as, for instance, in tetrahedrally bonded liquids such as SiO_2 or H_2O in which the local coordination is known to change with density. The empirical observation that fragility may vary with *pressure* [3,13] is a consequence of the possible change in the relative contributions to slowing-down due to T and to ρ . Indeed, the steepness index at constant pressure, $m_{P,\tau}$, defined by an equation similar to eq. (2) is related to that at constant density through

$$m_{P,\tau}(P) = m_{\rho,\tau}(1 + \alpha_P/|\alpha_\tau|), \quad (3)$$

where $\alpha_P = -\rho^{-1}(\partial\rho/\partial T)_P$ and $\alpha_\tau = -\rho^{-1}(\partial\rho/\partial T)_\tau$ are the isobaric and isochronic coefficients of expansivity; the ratio $\alpha_P/|\alpha_\tau|$ characterizes the relative effect of ρ over that of T at constant P when $\tau_\alpha = \tau$ [14]. $(1 + \alpha_P/|\alpha_\tau|)$ is also equal to $\frac{H_P}{E_V}$ [15], with $H_P = (\partial \ln(\tau_\alpha)/\partial(1/T))_P$ and $E_V = (\partial \ln(\tau_\alpha)/\partial(1/T))_\rho$. One can see from eq. (3) that the fragility measure at constant P is always larger than the constant- ρ fragility: from the estimated values of the ratio $\alpha_P/|\alpha_\tau|$, we obtain, *e.g.*, at $P = 1$ atm and $\tau = 1 - 100$ s, $m_{\rho,\tau} = 61$ and $m_{P,\tau} = 95$ for PVAc, $m_{\rho,\tau} = 46$ and $m_{P,\tau} = 75$ for PECH, $m_{\rho,\tau} = 51$ and $m_{P,\tau} = 75$ for

PVME, $m_{\rho,\tau} = 64$ and $m_{P,\tau} = 77$ for 1,4-PB, $m_{\rho,\tau} = 38$ and $m_{P,\tau} = 40$ for glycerol, and $m_{\rho,\tau} = 45$ and $m_{P,\tau} = 82$ for o-TP. In addition, the variation with P of the fragility $m_{P,\tau}$ depends on that of the ratio $\alpha_P/|\alpha_\tau|$; the amplitude and the sign of this latter is species-specific: for instance, it has been shown to decrease with increasing P in the case of glycerol (resulting in a decrease of the fragility with pressure [13]) and to increase with P in the case of 1,4-polybutadiene [14]. Combining eq. (1) and eq. (3) gives $\alpha_P/|\alpha_\tau| = \alpha_P \frac{d \ln(e(\rho))}{d \ln(\rho)} T_\tau$, which in the case of a power law behavior $e(\rho) = \rho^x$ simply reduces to $\alpha_P \cdot x \cdot T_\tau$, where both α_P and T_τ depend on P ; usually α_P decreases with P [16] and T_τ increases with P , leading to a variety of behaviors for $\alpha_P/|\alpha_\tau|$ (see above).

The fact that fragility is an intrinsic property of a glass-former is best represented by modifying the now standard Angell plot [2] in which $\log(\tau_\alpha)$ is shown *vs.* the inverse scaled temperature T_g/T at constant (usually atmospheric) pressure: we suggest instead, when enough data is available, to plot $\log(\tau_\alpha)$ *vs.* X/X_g , where $X = e(\rho)/T$ is the scaling variable introduced above and X_g its value when τ_α reaches a characteristic “glass transition” value, say $\tau_\alpha = 100$ s for dielectric relaxation data. The steepness of the $\log(\tau_\alpha)$ -*vs.*- X/X_g curve is a measure of the intrinsic fragility of a system, since indeed, according to eq. (1),

$$m_X = \left. \frac{d \log(\tau_\alpha)}{d(X/X_g)} \right|_{X=X_g} = X_g F'(X_g) \quad (4)$$

is equal to $m_{\rho,\tau}$ at the chosen glass transition point. The modified Angell plot is shown in fig. 4, where all the polymer data considered in this study (see inset of fig. 4) are displayed together with results for a “fragile” liquid o-TP and an “intermediate” one, glycerol [4]. (Note that the estimated values of m_X , respectively, 54, 55, 50, 59, 38, 47 for PVaC, PECH, PVME, 1,4-PB, glycerol, and o-TP, are within 10–15% of the values of $m_{\rho,\tau}$ given above, which is reasonable considering the various experimental error bars.)

In conclusion, we have shown that the P - and T -dependences of the α -relaxation time of glass-forming polymers and liquids can be combined, after conversion to ρ - T data, in a function of a single scaling variable $X = e(\rho)/T$, where $e(\rho)$ is well fitted by a power law ρ^x , x being species-specific [17]. On the practical side, this provides a simple way to organize and display the increasing amount of isobaric and isothermal relaxation time data on glass-forming polymers and liquids. On the theoretical side, this suggests that fragility is an intrinsic property of a glass-former, which is best illustrated on a modified Angell plot $\log(\tau_\alpha)$ *vs.* X/X_g , and that $e(\rho)$ characterizes the density dependence of the “bare” activation energy scale.

* * *

We would like to dedicate this letter to our late coworker and friend DANIEL KIVELSON whose stimulating presence and creative thinking we miss very much.

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